

Synthesis and Luminescence Properties of ZnO Nanoparticles Produced by the Sol Gel Method

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ABSTRACT

This paper reports on the synthesis of ZnO nanoparticles with 20-30 nm size and spherical morphology using Sol Gel method. Sols were prepared by dissolving Zinc Acetate in Methanol. Systematic study of the key parameters (precursor, concentration, heat treatment conditions) has been taken into account, the best concentration of each precursor was adjusted to get the optimum results. X-ray diffraction analysis (XRD) was used to determine the crystallinity, particle size and lattice parameter. Scanning electron microscopy (SEM) of the sample reveals the formation of ZnO nanoparticles. Room temperature Photoluminescence (PL) measurement of the sample was done to understand the nature of possible defect level transitions responsible for rarely observed visible luminescence in ZnO. This study reveals the usefulness of the ZnO nanoparticles as a luminescent material.

Keywords: ZnO nanoparticles, Sol Gel Synthesis, Luminescence.

1. INTRODUCTION

As one of the prominent material in the metal oxide family nanostructured ZnO, because of its large band gap (3.37 eV at room temperature) and high exciton binding energy (60 meV), has been intensely studied for its versatile physical properties and promising potential¹.

ZnO nano particles can be prepared by different methods. In order to extend the domain of our research and to meet the industrial needs of large scale production, herein, we report the synthesis of ZnO nanoparticles by hydrolyzing Zinc Acetate in alcohol solutions using Sol Gel method.

Sol gel is one of the most efficient chemical route which presents an easy way

of preparing nanomaterials with reliability, repeatability and simplicity, and the particle size can be controlled by further heat treatment.

However, ZnO nanoparticles produced via wet chemical route have low chemical and thermal stability resulting in alteration of originally optimized parameters due to aggregation process or chemical reaction with the surrounding which limits the practical application of these nanosystems². The Sol-gel process using Zinc Acetate has proved to be a relatively simple method for synthesizing ZnO nanoparticles with a narrow size distribution and excellent crystallinity³.

Generally, ZnO can emit three luminescence bands in the ultraviolet (UV), green, and yellow spectral range, the 3.3 eV UV emission has been well understood to be due to the excitonic recombination. For the emission in the visible however the exact mechanism is still in controversy inspite of the various mechanisms proposed by many groups⁴⁻⁵.

In this work we have prepared ZnO nanoparticles simply by hydrolyzing Zinc acetate in alcoholic solution by sol gel method and studied the usefulness of as formed nanoparticles as a luminescent material. X-ray diffraction (XRD) patterns, DSC-TGA analysis and scanning electron microscopy of the sample were also investigated.

2. EXPERIMENTAL

2.1 Synthesis

For this study, ZnO nanoparticles were prepared using Zinc Acetate

[Zn(CH₃COO)₂ · 2H₂O] as precursor and Methanol (MtOH) as solvent. 2.195 gm of Zinc Acetate was dissolved into 1M of MtOH then the mixture was stirred vigorously at 50⁰C for 1.5 hour small amount of water was added to start hydrolysis. After stirring the solution becomes translucent milky and viscous after cooling the solution was aged for one week, after one week no cracks in the gel were observed. Then the sample was heated upto 400⁰ C for the removal of residual organics and formation of crystalline phases to form the final product. The final product is then characterized by X-ray diff analysis(XRD), Scanning Electron Microscopy (SEM) and Photoluminescence Spectroscopy (PL analysis).

2.2. Characterization

X-ray diffraction and phase identification as synthesized ZnO nanoparticles was performed on Rigaku Miniflex II deffractometer with CuK α target ($\lambda=1.54060$ Å) at room temperature. The X-ray generator was operated at 30kV, XRD patterns were recorded in the 2 θ range from 0-80⁰ with a scan speed of 2⁰ per minute. The refinement of the X-ray results was done using *Match* and *PowderX* software. The surface morphology of the as prepared sample was obtained on JEOL JSM 6390 scanning electron microscope. Room temperature photoluminescence spectrum of the ZnO nanoparticles was recorded with 330 nm excitation on a Hitachi F-7000 Spectrophotometer equipped with Xenon pulsed lamp.

3. RESULT AND DISCUSSION

3.1 XRD results

XRD pattern of ZnO nanoparticles synthesized by sol gel method is shown in fig. 1 all detectable peaks could be clearly identified and indexed as the Hexagonal

Zinc Oxide structure found in reference data (JCPDS: 36-1451), this fact indicates that the as synthesized product is Pure crystalline Hexagonal Zinc Oxide (space group $p6_3mc$), no peaks related to any intermediate product or Zinc hydroxide is observed. Indexing and refinement of the diffraction data was done using Match and PowderX software.

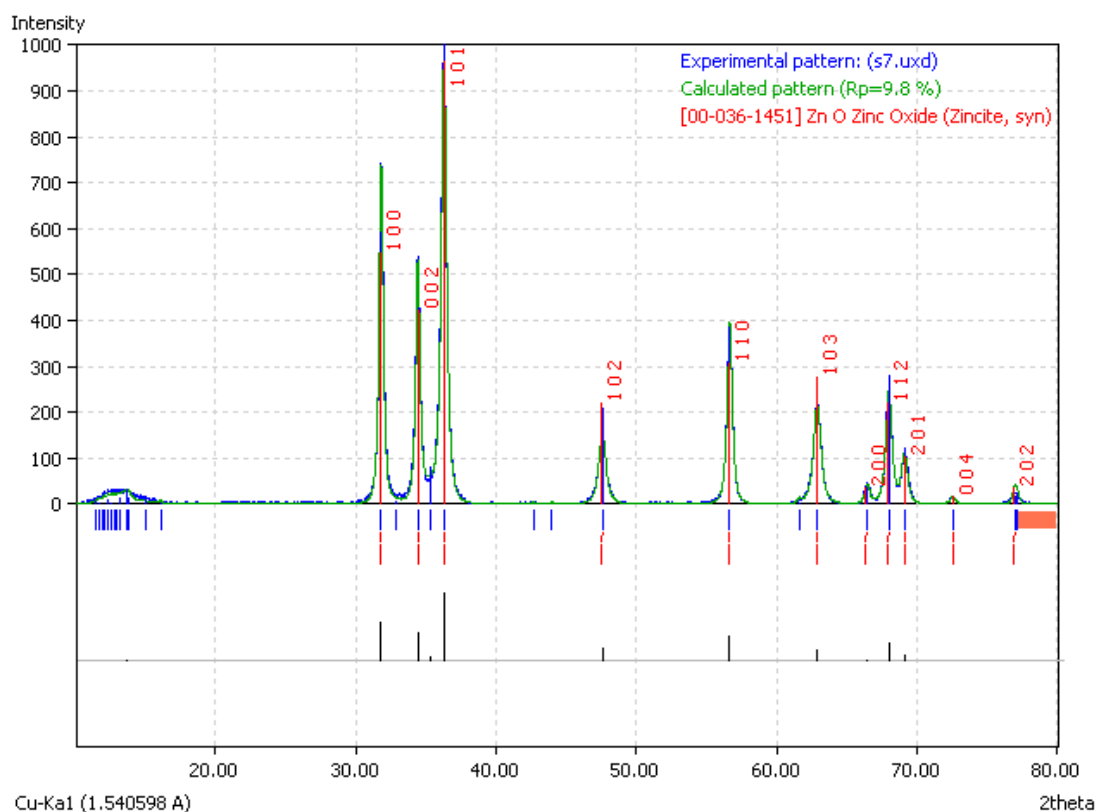


Fig. 1 X-Ray diffraction pattern of ZnO nanoparticles synthesized by Sol Gel method (profile fitting is done using Match software.)

From 2θ values, the inter planer spacing d is calculated and a good agreement between observed and theoretically calculated values is found to exist.

The apparent crystallite size can be calculated using Scherrer's Formula Given by Eq.(1)

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where $k = 0.94$, β is FWHM, θ is the Bragg's angle and λ is the wave length of the X-ray used ($CuK\alpha = 1.540 \text{ \AA}$) and the average crystalline size was found to be in the range of 20-30 nm.

3.2 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) of the sample was done using JEOL JSM 6390 electron microscope. The

morphology of the final product after drying to Xerogel and subsequent heating up to 400°C is shown in fig. 2(a) (b) with different magnifications.

The growth and evolution of such nanoparticle systems can be considered as a function of temperature treatments. Considering this factor, the Xerogel was heated very slowly for the removal of the residual organics upto 400°C with linear temperature increments.

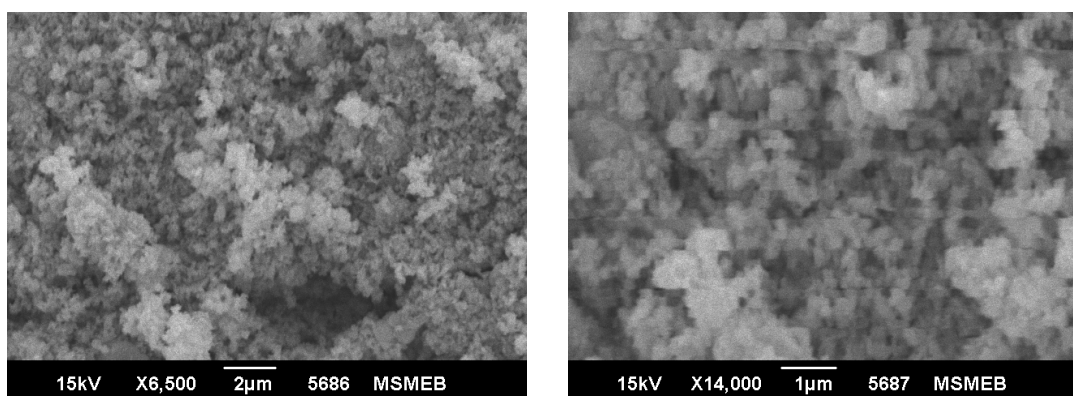


Fig 2. (a)- (b) SEM images of ZnO nanoparticles at different magnification

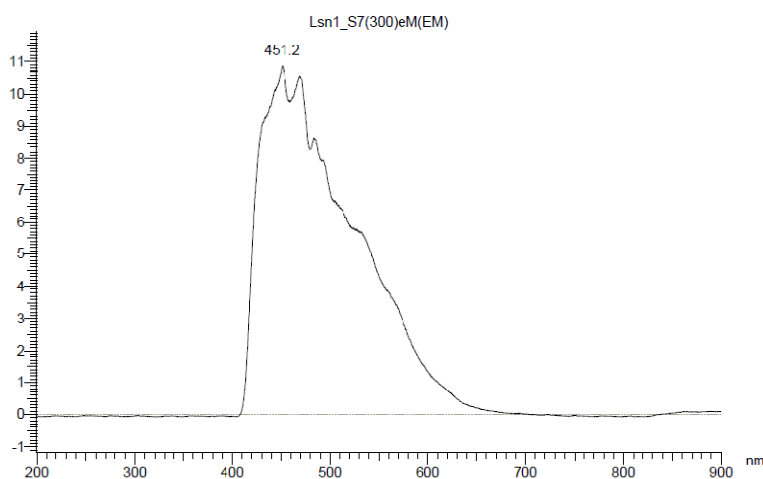


Fig 3. Room temperature PL spectra of ZnO nanoparticles

It is revealed by fig 2(a) - (b) that the product consists of nanoparticles of nearly spherical morphology, the size of the nanoparticles is in good agreement with the results obtained by X-ray diffraction pattern.

3.3. Photoluminescence studies

The photoluminescence (PL) spectrum of the ZnO nanoparticles was recorded with a view to understand the effect of the formed nanoparticles on the emission properties of the material. Commonly known room temperature PL spectra of ZnO usually show three major peaks: an ultraviolet UV emission peak around 380 nm, a green emission peak around 520nm and a red or orange emission peak around 600 nm⁵.

Room temperature PL spectrum of the synthesized sample was recorded with 300 nm excitation (Fig 3). PL emission curve of as formed ZnO nanocrystals has a broad visible emission band extending from 400 nm to 700 nm nearly covers the entire visible range showing two dominant blue emission peaks at 451nm and 469 nm. The broadness of the band represents the synchronous superposition of many different deep level emissions. A small variation in the emission spectrum is observed at 530 nm represent the contribution of green band in the emission spectra. It is clear that the ZnO can emit luminescence over the entire visible range. Radiative transition⁶, impurities and defect states (native point defects) can be considered as plausible explanation of the PL emission in the given sample⁷.

Emission lines at 405, 420, 446, 466, 485, 510, 583, and 640 nm have already been reported in the literature⁸. Which have

been attributed to the defect level emission in ZnO.

Commonly identified native defects in ZnO are Oxygen vacancies (V_o), Zinc vacancies (V_{Zn}), Oxygen interstitials (O_i), Zinc interstitials (Zn_i), Oxygen antisites (O_{Zn}), and Zinc antisites (Zn_o). The concentration of these deep levels or native point defects in ZnO depends on their formation energy and at thermodynamic equilibrium the concentration can be given as⁹.

$$C = N_{sites} \exp \left[-\frac{E^f}{k_B T} \right]$$

Where c is the point defect concentration, N is the no of available sites to accommodate the defect, k_B is the Boltzmann's constant and T is the temperature.

The blue emission band observed in the ZnO nanocrystals at 451nm and 469 nm can be attributed to oxygen vacancies, the formation energy of an oxygen vacancy depends on the abundance of the oxygen and the zinc atom in the growth environment⁷ so the growth environment controls the concentration of native defects in ZnO.

The green emission observed at around 530 nm is attributed to Oxygen vacancies and Zinc Interstitials, the green emission band has been explained as originating from more than one deep level defect. This luminescence band appears at the energies of 2.4-2.5 eV is found to be observed because of the transition from conduction band to V_o or to V_{Zn} or to both V_o and V_{Zn} ^{7, 10}.

For the present sample NBE excitonic UV emission is not observed. This band is expected to be suppressed by the structural variation in the sample, when the

ZnO nanostructures are heat treated in air ambient environment, some of the oxygen vacancies are expected to be removed and the free charge density in ZnO decreases under this condition the electrons excited to the conduction band will move towards the central bulk region^{11,12} these electron are very likely to be relaxed to a defect level via radiative recombination and at the same time the UV band edge intensity is either greatly reduced which may be the reason for the suppression of the UV band edge emission in the PL spectra.

4. CONCLUSION

In the present study ZnO nanoparticles were synthesized via Sol Gel route, XRD of the material confirms the formation of ZnO (JCPDS 36-1451), morphology of the particles were found to be spherical. PL emission of the sample nearly covers the full visible range attributed to the deep level emissions which can be considered to be promoted by the morphology and size of nanoparticles formed. Considering the growth and reproducibility of the ZnO nanoparticles visible emission found in the as formed sample provides potential for application of this material in LED applications.

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